Solutions for Chemical Hydrogen Storage: Hydrogenation/ Dehydrogenation of B-N Bonds

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Project ID # ST4

Overview

Timeline

- Start: FY 05
- End: FY 09
- 25% complete

Budget

- Total funding
  - $1.1 M DOE share
  - $ 0.28 M cost share
- DOE FY05: $155K(partial)
- DOE FY06: $ 200 K

Barriers

- Weight and volume
- Efficiency
- Regeneration Processes

Amineboranes offer high H_2 storage capacity in principle, but thermal H_2 release is slow and inefficient. Effective catalysts for dehydrogenation/hydrogenation of BN compounds are needed.

Partners

DOE Center of Excellence for Chemical Hydrogen Storage

Objectives

- To understand the interaction of BN compounds with transition metals
- To develop Platinum group metal(PGM) based catalysts for dehydrogenation and rehydrogenation of BN compounds
- To determine thermodynamic parameters for hydrogenation/dehydrognation
- To develop non PGM catalysts

Ammonia Borane as a H_2 Storage Material

Appropriate Thermodynamics

$$n\ H_3NBH_3 \longrightarrow [H_2NBH_2]_n + n\ H_2 \qquad \Delta H_{calc} = 8\ \text{kcal.mol}^{-1}$$

$$[H_2NBH_2]_n \longrightarrow [HNBH]_n + n\ H_2 \qquad \Delta H_{calc} = -3\ \text{kcal.mol}^{-1}$$

$$[HNBH]_n \longrightarrow [NB]_n + n\ H_2 \qquad \Delta H_{calc} = -9\ \text{kcal.mol}^{-1}$$

Near thermoneutral reactions important for reversibility.

Dixon, D. A.; Gutowski, M. *J. Chem. Phys. A* **2005**, *109*, 5129.

Ammonia Borane as a H_2 Storage Material

DOE Storage Targets

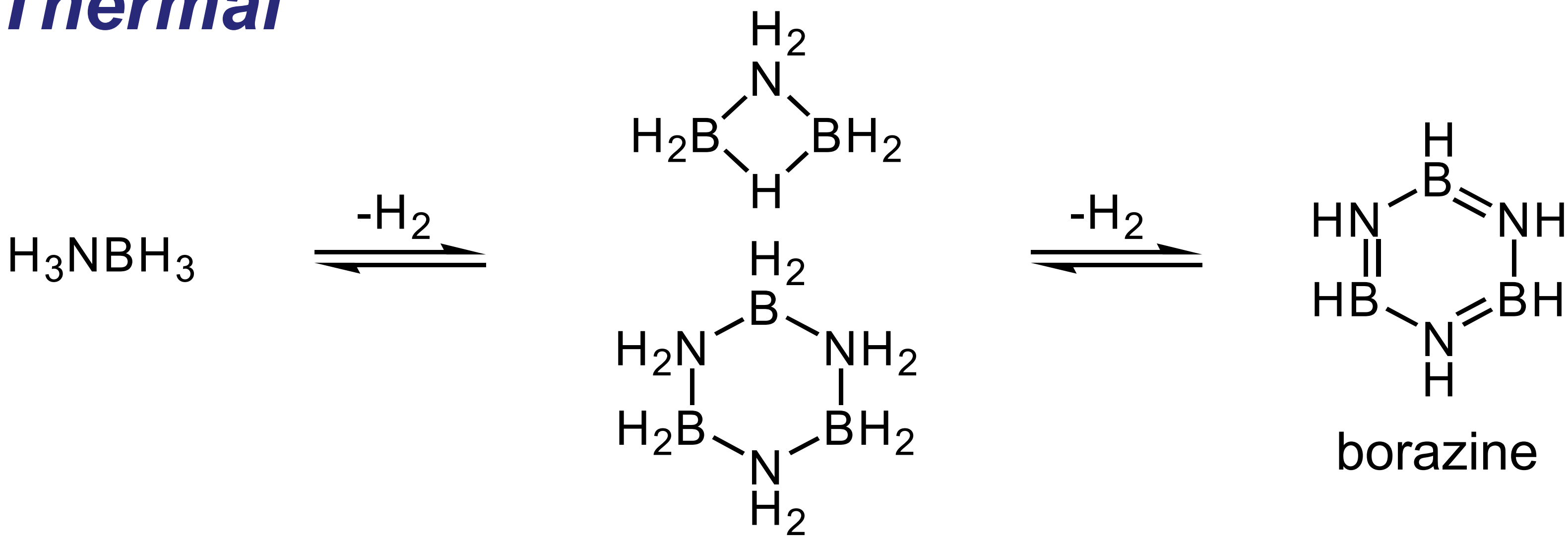
	2010	**2015**
Target wt%	6.0	9.0

Storage Potential of Ammonia Borane

H_2 Released	**1**	**2**	**3**
Wt% H_2	6.5	13.0	19.6
Product	$[H_2NBH_2]_n$	$[HNBH]_n$	$[NB]_n$

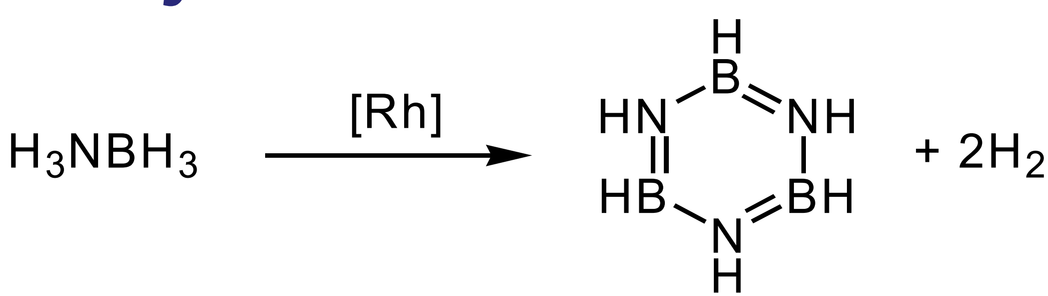
Dehydrogenation of Ammonia Borane

Thermal



Wang, J. S.; Geanangel, R. A. *Inorg. Chim. Acta* **1988**, *148*, 185.

Catalyzed



0.6 mol% catalyst

48 – 84 hours at 45 ºC

Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776.

Approach

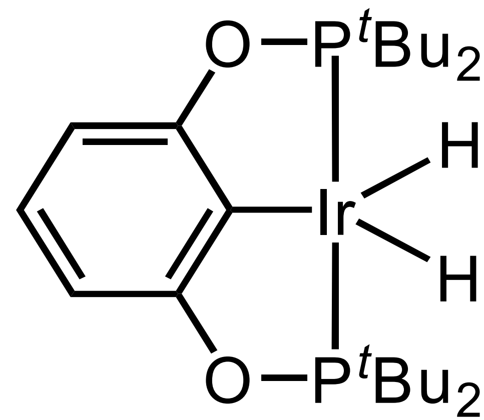
- We seek to develop catalysts to accelerate dehydrogenation/rehydrogenation of amine boranes, eg.

$$n\ NH_3BH_3 \overset{[\text{catalyst}]}{\rightleftharpoons} [NH_2BH_2]_n + n\ H_2$$

Results: Catalyst Choice

$$n\ \mathrm{NH_3BH_3} \xrightarrow[\text{THF, rt}]{\text{[catalyst]}} [\mathrm{NH_2BH_2}]_n + n\ \mathrm{H_2}$$

- $(POCOP)Ir(H)_2$ already known to be an effective *alkane* (transfer) dehydrogenation catalyst.
- Amineboranes are isoelectronic with alkanes.

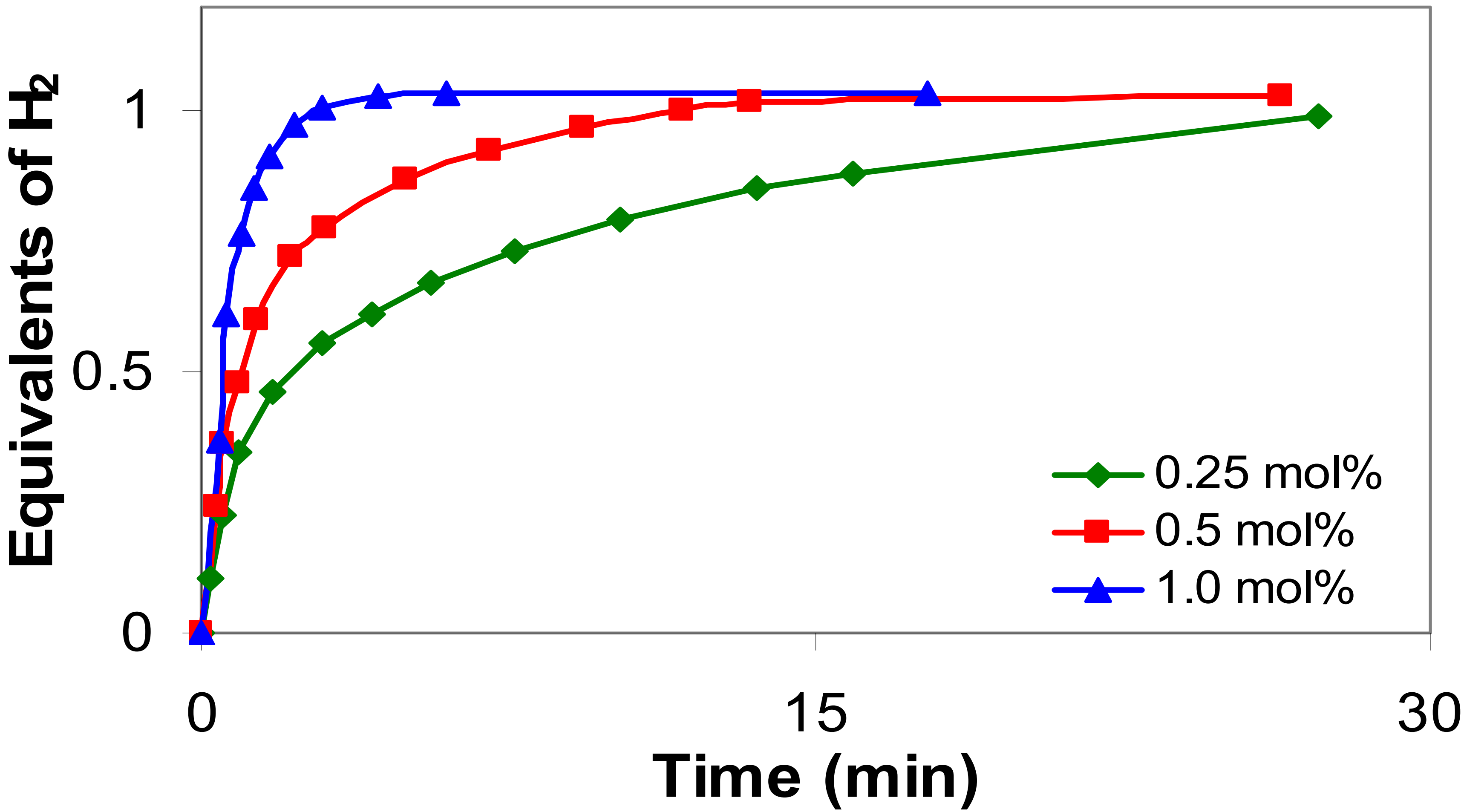


"(POCOP)Ir(H)$_2$"

Brookhart, M. *et al. J. Am. Chem. Soc.* **2004**, *126*, 1804.

Evolution of Hydrogen

$$n\, H_3NBH_3 \xrightarrow{[Ir]} [H_2NBH_2]_n + n\, H_2$$

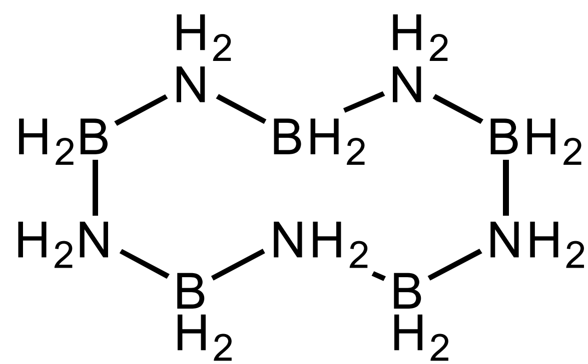


Characterization of Solid Product

$$n\ \mathrm{NH_3BH_3} \xrightarrow[\text{THF, rt}]{\text{[catalyst]}} \boxed{[\mathrm{NH_2BH_2}]_n} + n\ \mathrm{H_2}$$

solid

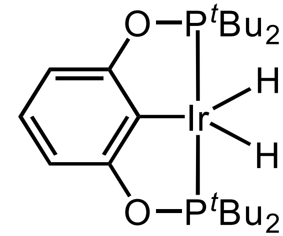
- Single well characterized non-volatile product
- All other reported reactions of this type lead to mixtures including borazine



$n = 5$

Böddeker, K. W.; *et al. J. Am. Chem. Soc.* **1966**, *88*, 4396

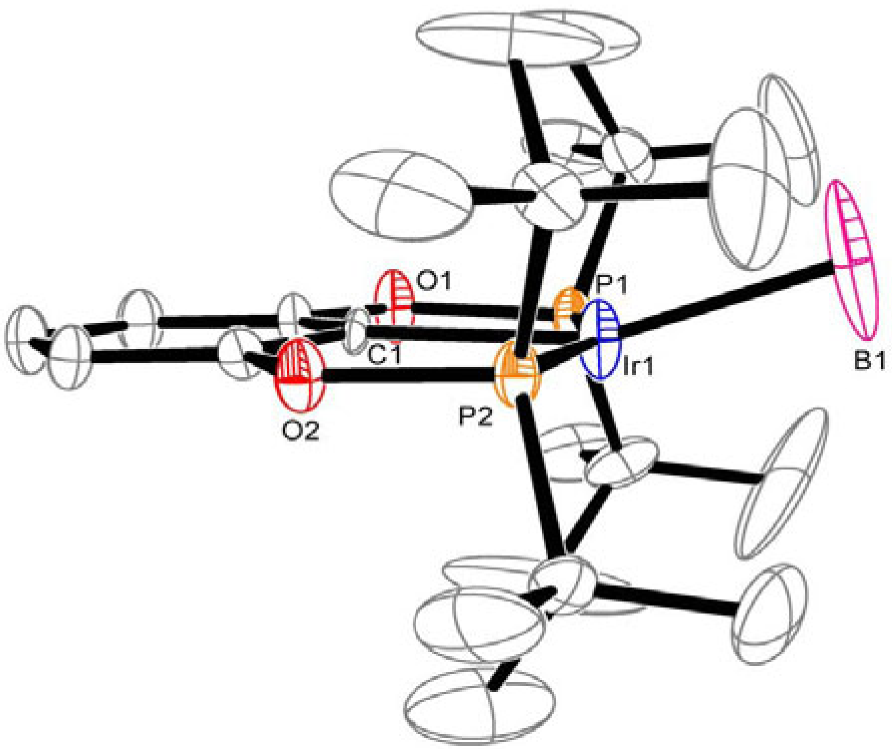
Comparison with Previous Best Catalyst

	$[Rh(1,5\text{-}COD)(\mu\text{-}Cl)]_2$	
Catalyst Loading	0.6 mol%	0.5 mol%
Temperature (ºC)	**45**	**25**
H_2 evolved (equiv.)	2	1
Products	Borazine	$[H_2NBH_2]_5$
Time	**48 – 84 hr**	**< 15 min**

At least 200 fold increase in reaction rate over previous best.

Manners *et al. J. Am. Chem. Soc.* **2003**, *125*, 9424.

- Eventually, the Ir catalyst converts to a dormant form:



Future Work

- In collaboration with PNNL, use calorimetry to accurately measure the heat of reaction for the dehydrogenation reaction. This is critical to validate computational work and to evaluate reversibility.
- Explore ligand variations with Ir for better catalysis.
- Define the mechanism of the reaction; use mechanistic insight to guide catalyst development
- Study rehydrogenation reactions.
- Develop non PGM catalysts with less expensive metals such as Fe, Co and Ni.

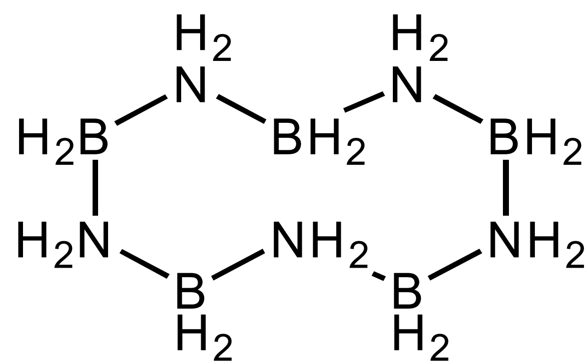
Summary

- We have developed an extraordinarily active dehydrogenation catalyst with activity orders of magnitude greater than the prior art.
- The catalyst is well defined and active indefinitely in the presence of hydrogen.
- In contrast to previous reports of complex mixtures, our Ir catalyst gives a single non-volatile BN containing product.

Backup Data: Characterization of Solid Product

$$n\ \mathrm{NH_3BH_3} \xrightarrow[\text{THF, rt}]{\text{[catalyst]}} \boxed{\underset{\textbf{solid}}{[\mathrm{NH_2BH_2}]_n}} + n\ \mathrm{H_2}$$

- Solid state ^{11}B NMR.
- Infrared spectroscopy.
- Powder X-ray diffraction.



$n = 5$

Böddeker, K. W.; *et al. J. Am. Chem. Soc.* **1966**, *88*, 4396

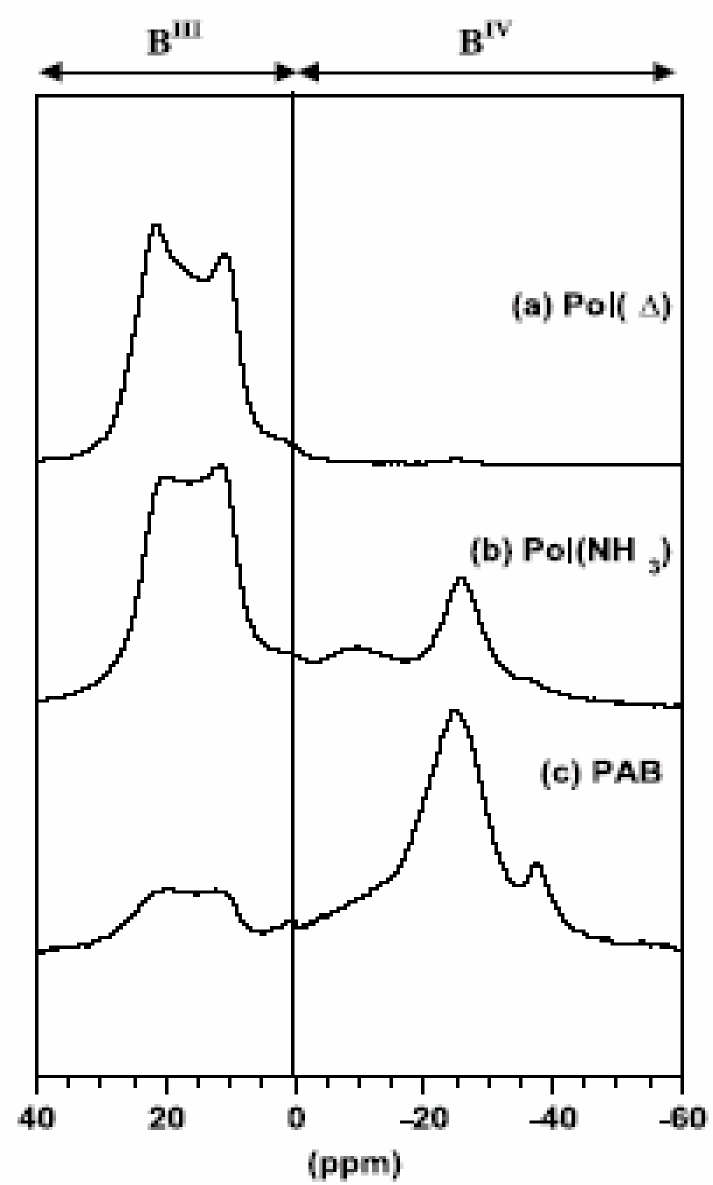


Fig. 5. ^{11}B MAS NMR spectra of the three polymers recorded at 9.4 T.

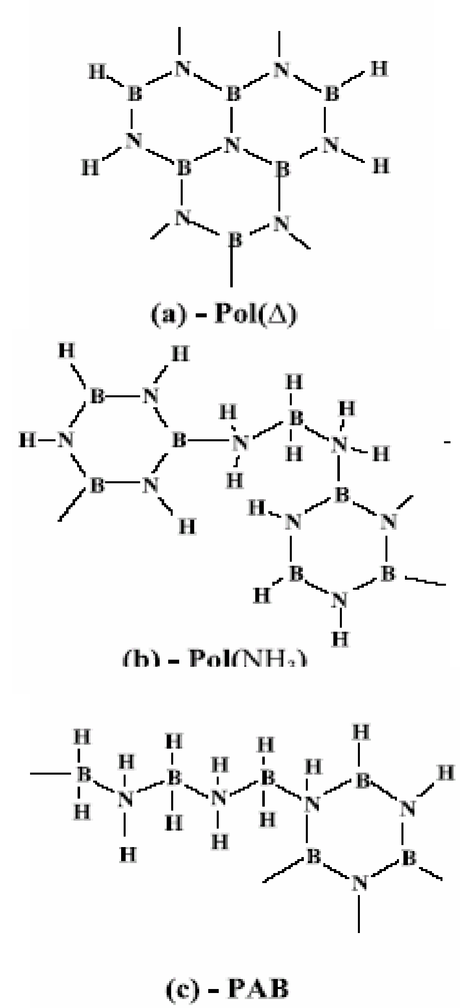
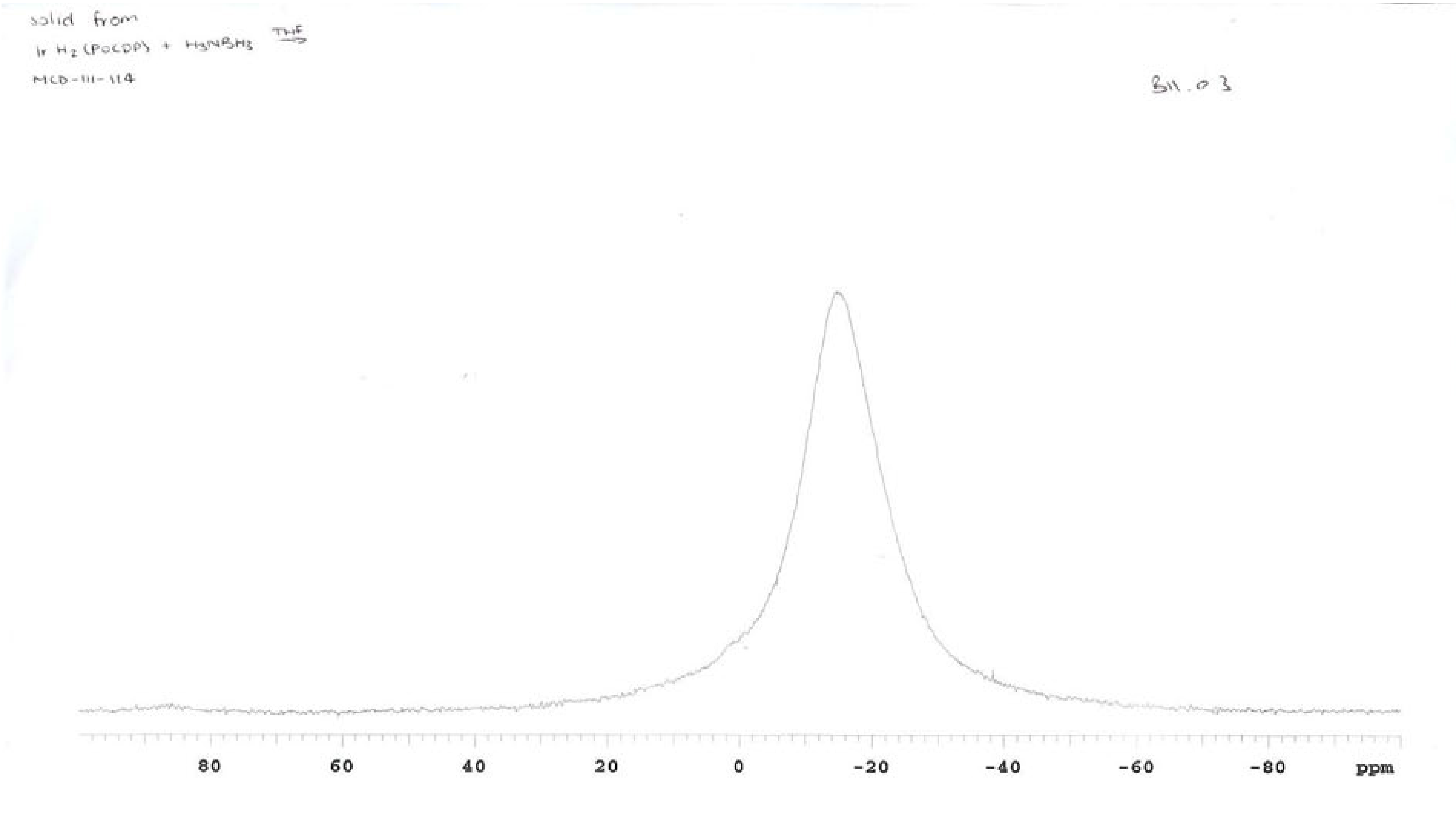


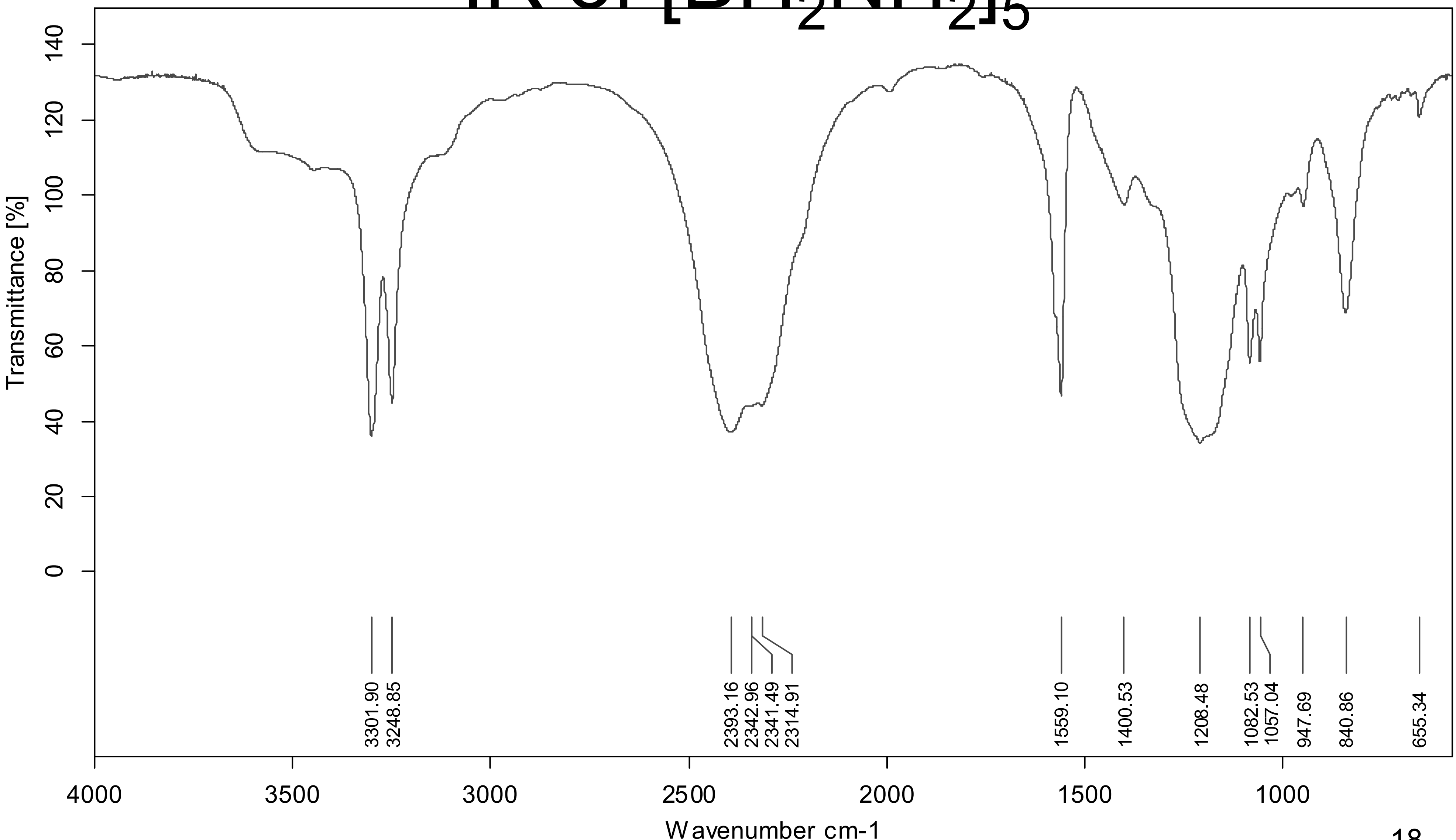
Fig. 8. Schematic representation of the three polymers structures, based on NMR results.

Gervais, C.; Babonneau, F. *J. Organomet. Chem.* **2002**, *657*, 75.

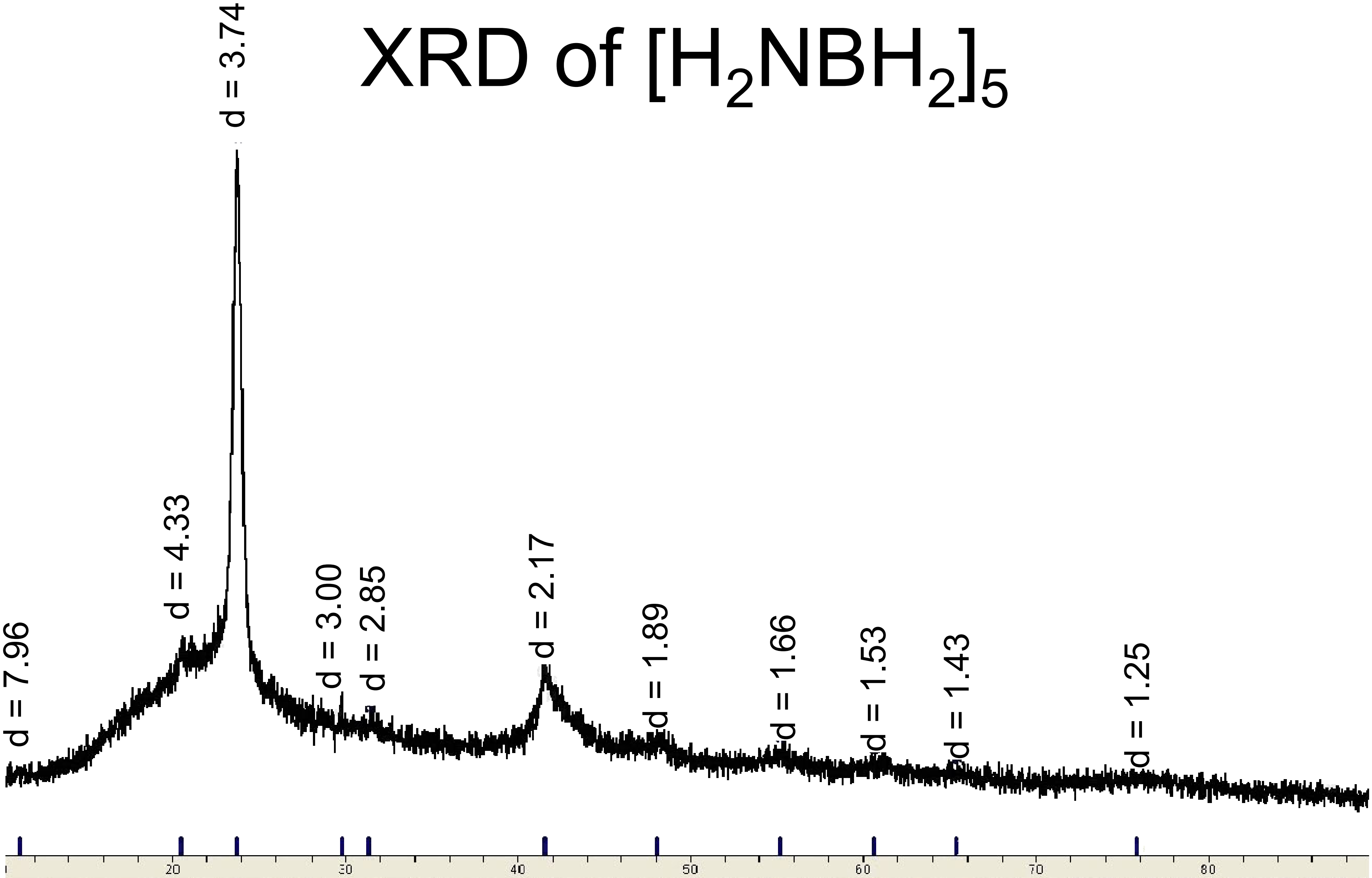
Solid State ^{11}B NMR of $[BH_2NH_2]_5$

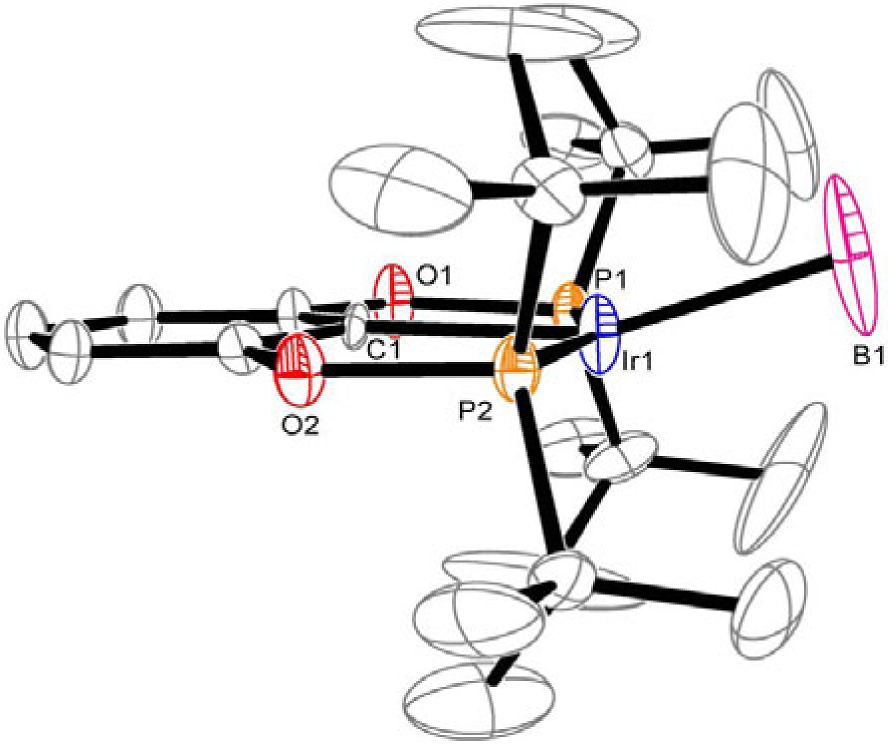


IR of $[BH_2NH_2]_5$

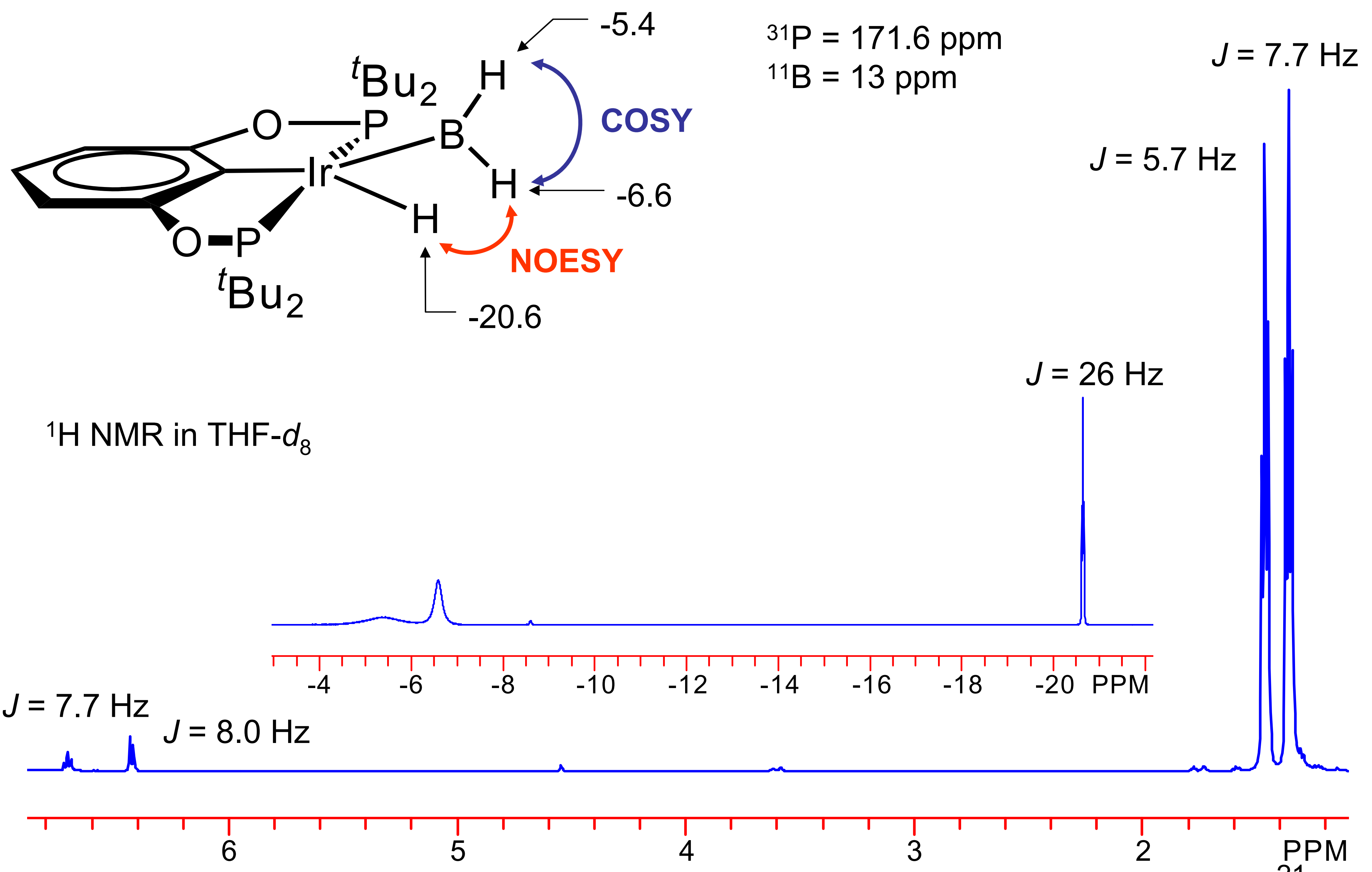


XRD of $[H_2NBH_2]_5$



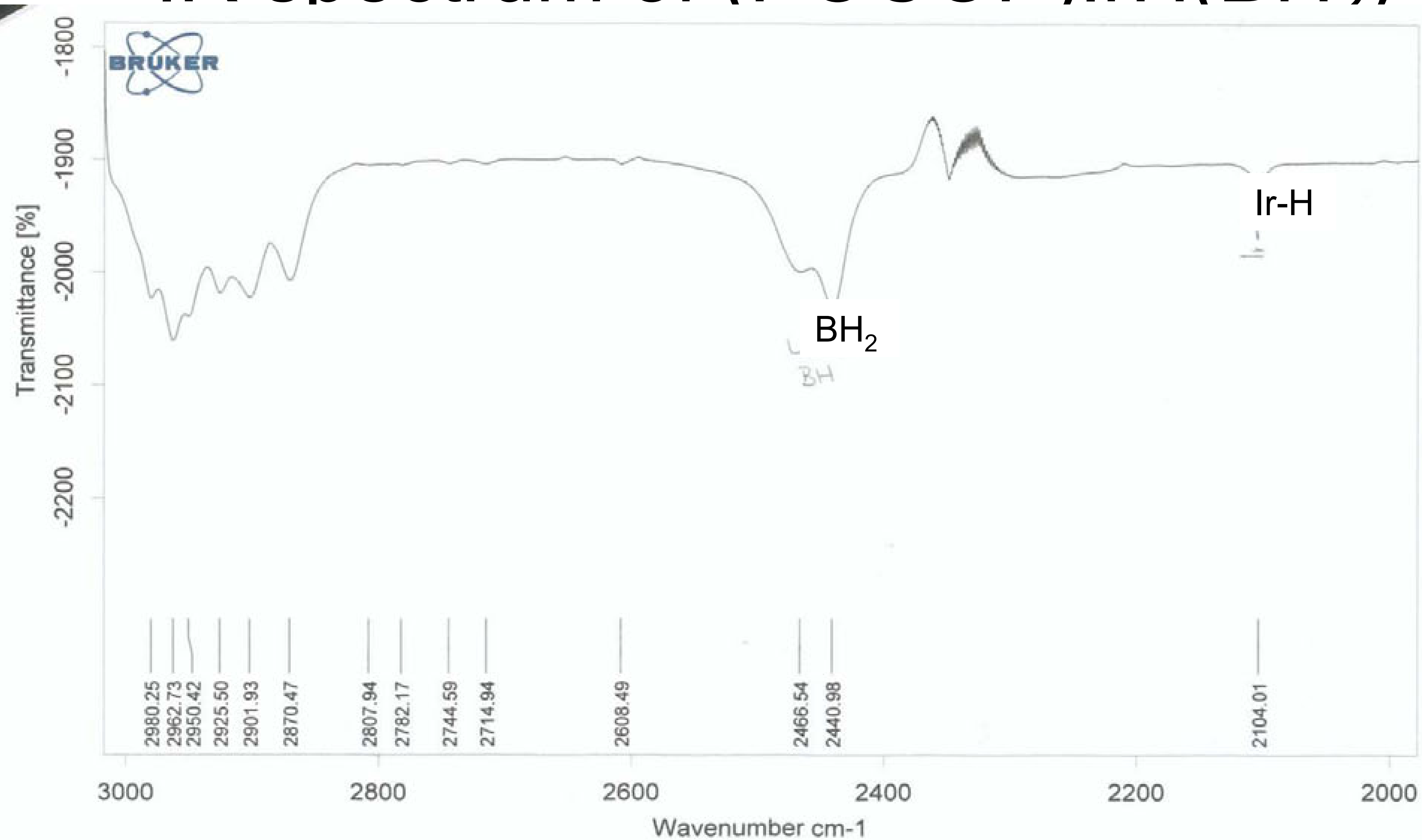


	Bond Length (Å)
Ir(1)-B(1)	2.185(9)
Ir(1)-P(1)	2.3137(14)
Ir(1)-P(2)	2.3122(14)
Ir(1)-C(1)	2.032(4)



-5.4
^{31}P = 171.6 ppm
^{11}B = 13 ppm
J = 7.7 Hz
tBu2
H
B
COSY
O
P
Ir
H
-6.6
J = 5.7 Hz
H
O
P
NOESY
tBu2
-20.6
J = 26 Hz
^{1}H NMR in THF-d_8
-4
-6
-8
-10
-12
-14
-16
-18
-20
PPM
J = 7.7 Hz
J = 8.0 Hz
6
5
4
3
2
PPM

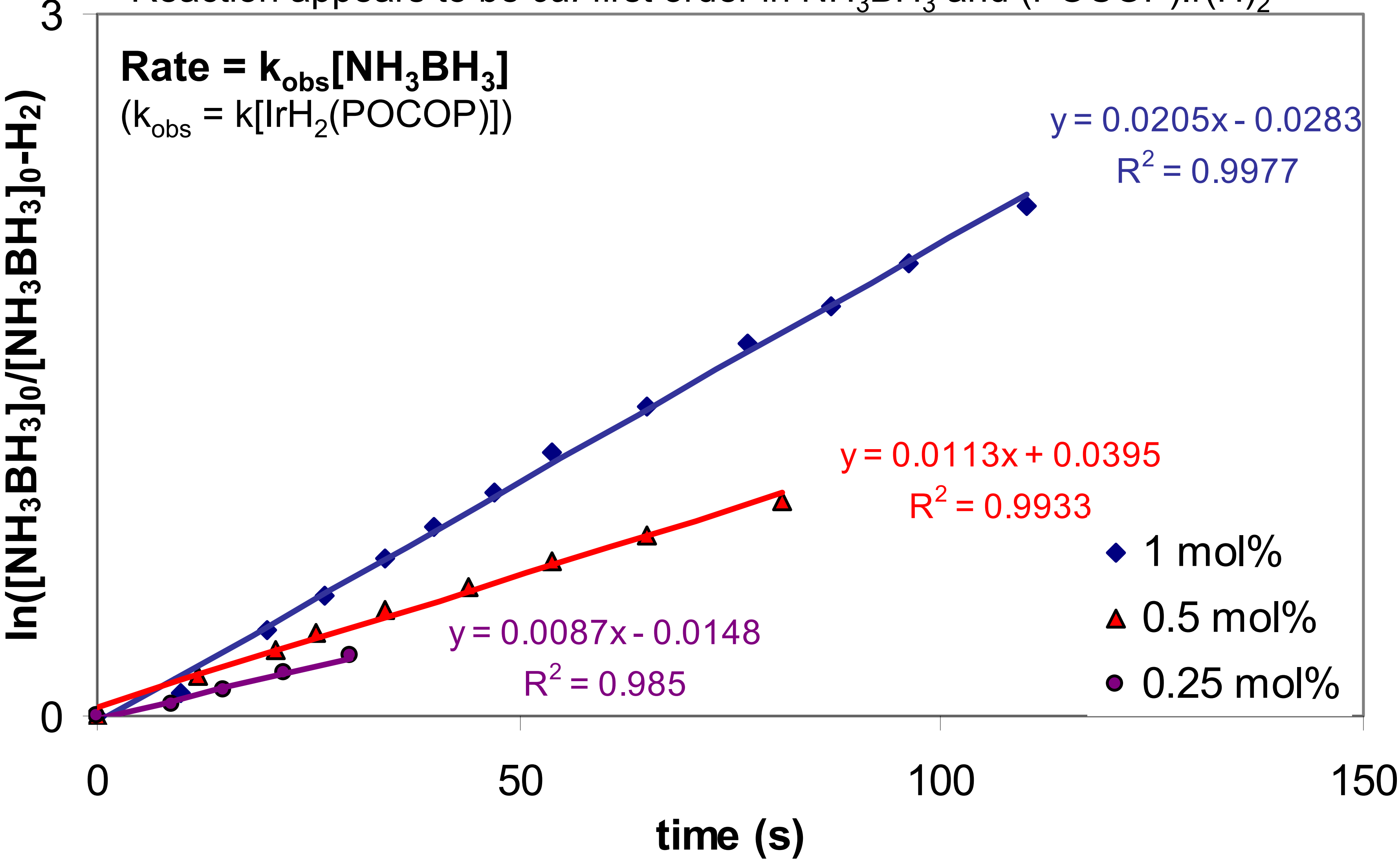
IR spectrum of (POCOP)IrH(BH_2)

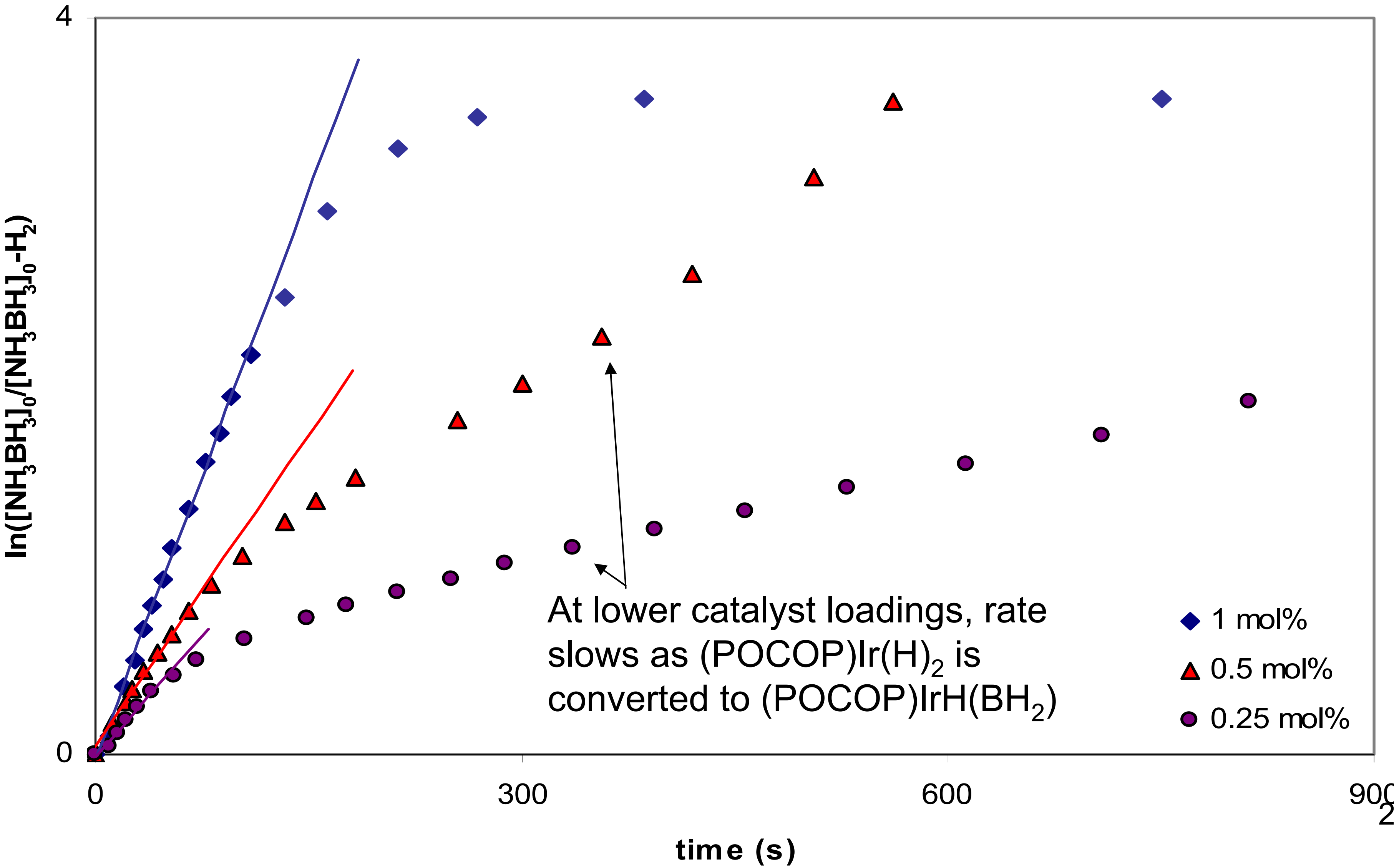


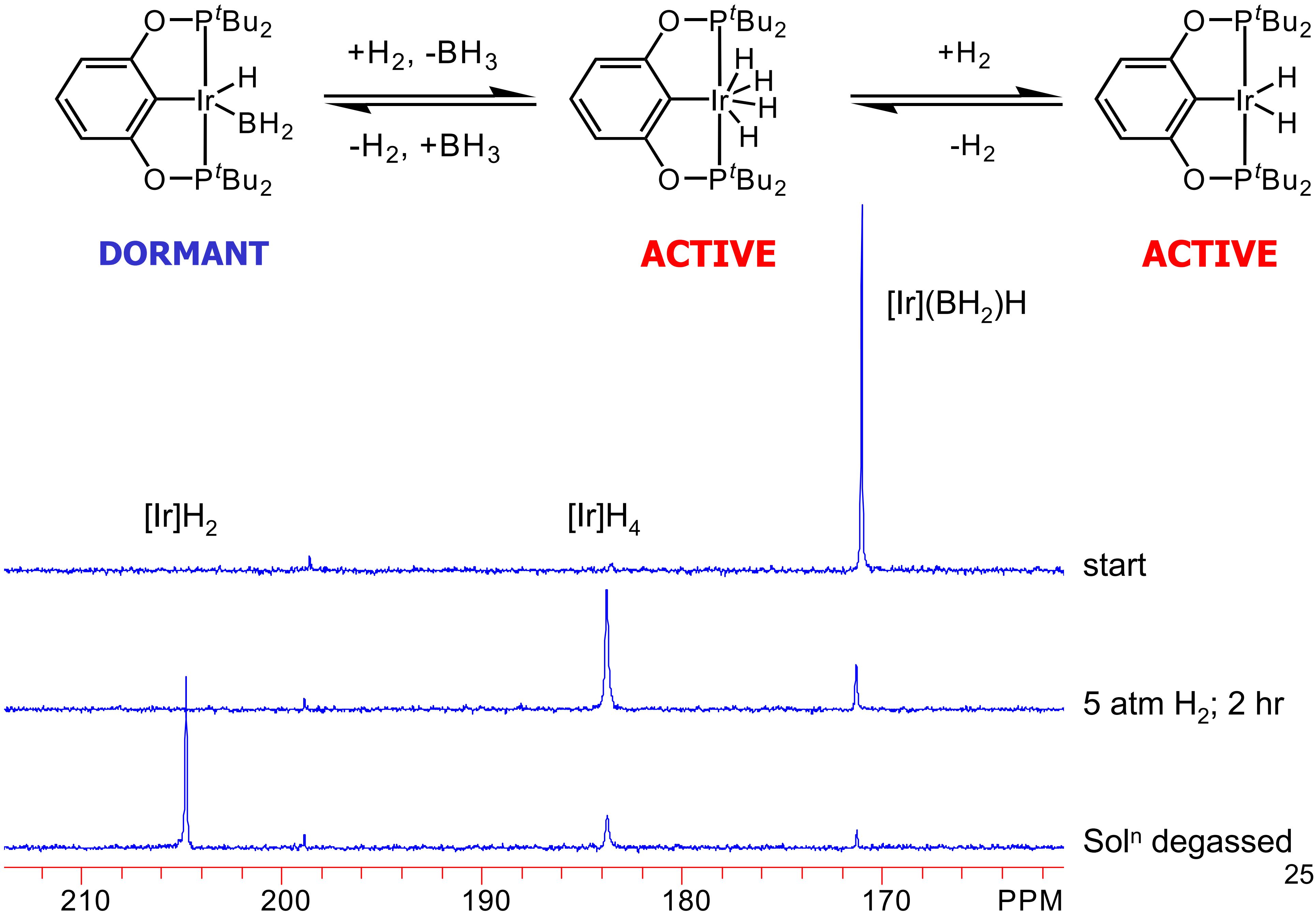
Solution in C_6H_6

Initial Rates

Reaction appears to be *ca.* first order in NH_3BH_3 and (POCOP)Ir(H)$_2$




4
0
$\ln([NH_3BH_3]_0/[NH_3BH_3]_0\text{-}H_2)$
0
300
600
900
time (s)
At lower catalyst loadings, rate slows as (POCOP)Ir(H)$_2$ is converted to (POCOP)IrH(BH$_2$)
1 mol%
0.5 mol%
0.25 mol%


+H2, -BH3
-H2, +BH3
+H2
-H2
DORMANT
ACTIVE
ACTIVE
[Ir](BH2)H
[Ir]H2
[Ir]H4
start
5 atm H2; 2 hr
Soln degassed
210
200
190
180
170
PPM

Publications and Presentations

Paper on the Ir catalyst submitted to J. Am. Chem. Soc.

Critical Assumptions and Issues

- Computational work suggests that the hydrogenation/dehydrogenation of BN compounds is reversible. This needs to be verified by experiment. Thermodynamic data for these complexes is very limited.
- The formation of volatile borazine must be avoided for fuel cell applications. Most catalysts generate mixtures including borazine.
- The cost of amine borane must be brought down.